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# nuclear science and technology

## Contaminated smoke: a simulation of heavy metal containing aerosols from fires in plutonium glove boxes

### Part II

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# 1. INTRODUCTION

An experimental investigation was undertaken to estimate, under realistic conditions, the potential airborne spread of radioactive contamination in the event of a glove box fire in facilities for fabrication of nuclear fuels.

For this purpose, a special fire chamber simulating a plutonium handling facility was developed with the aim of studying the dispersion and transport of the heavy metal during glove box fires on a full-size laboratory scale. Since radioprotection considerations preclude the use of plutonium in large-scale experiments, cerium, a chemically similar element, was used as a substitute.

The first step of this work, already reported (1), dealt extensively with fires of PMMA (polymethylmethacrylate) "contaminated" with heavy metal oxide powder. This is the most usual scheme combining the major glove-box construction material with the normal surface contamination process during nuclear fuel fabrications, whereby plutonium and uranium compounds are usually handled (ballmilled, blended, pressed, sintered etc..) in the form of powder or pellets.

Thus a 0.6 MW PMMA fire source was standardized, the percentages of the airborne contamination carried away with the combustion gases and those remaining inside the fire chamber were measured, and the mechanisms of the resuspension, due to fire, and the transport of the heavy metal particles were investigated.

In "chemical" glove boxes, another frequent contamination process is the deposition and the subsequent drying inside the containment of droplets originating from aqueous, mostly acid, plutonium solutions.

The present report completes the study. On the one hand, fire experiments with contaminated specimens of other materials (both combustible or non-combustible), used in or on glove boxes, are described and compared with those with PMMA. On the other hand, the influence of the surface contamination from solution deposition is investigated. For simplification, the two contamination processes will be designated as "dry" (from powder) and "wet" (from solution).

Further, in spite of many attempts, conclusive particle size measurements of the contaminated smoke had been till now hampered because the too low concentra-

tion of the airborne heavy metal. A new, more sensitive, high volume cascade impactor was tested in this second part of the study.

## 2. EXPERIMENTAL

### 2.1. Equipment

The experiments were carried out in the fire chamber and with the analytical equipment which was already described in the first report (1). A ventilation rate of 2000 m3/h was applied which corresponds to the practice in the hot laboratories in the Joint Research Centre, Karlsruhe.

For comparative fire studies, we used the standard PMMA-fuel stack with the plate-shaped structure described in (1) which supplies a reproducible fire source of 0.6 MW peak intensity. The required samples of test material are located on the top of the stack, in the shape of an additional plate, 100 mm above the top PMMA plate. Soft materials (e.g. neoprene sheet) are supported by a steel wire arrangement.

### 2.2. Materials

Apart from the PMMA, the following materials, widely used for the construction and equipment of glove boxes, were involved in the comparative test fires: polycarbonate, polyethylene, neoprene (for the gloves), stainless steel (painted or not), aluminium, plywood and Kleenex (actually in cardboard containers). Because of their hyghly corrosive combustion products, fire experiments involving PVC (another major glove box material) and hypalon (special gloves) could cause severe damage to the ventilation system and the analytical equipment, and therefore require particular safety arrangements which are discussed in a separate paragraph.

## 2.3. Methods

The "dry" surface contamination process, i.e. spreading of the mixed cerium-europium oxide powder (with 16% europium and 64% cerium) was already described. It may be recalled that europium was added mainly to increase the sensibility of neutron activation analysis to determine the amount of contaminant in the collected aerosol samples.

The "wet" contamination process was simulated by evaporating an acid cerium-europium solution previously spread out uniformely on the test plate. This solution was made by dissolving ammonium cerium(IV) nitrate and europium(III) oxide in nitric acid to a final acidity of 1.1 N and a Ce/Eu ratio of 5 .

## 2.4. Special procedure for PVC and Hypalon

To neutralize the corrosive hydrochloric acid released during the combustion of these materials and stagnant or deposited in the fire room, a large excess of ammonia (for instance 2.5 Kg NH3 for 1 Kg PVC, i.e. about five times the stoichiometric amount) is rapidly injected into the chamber immediately after complete burning of the fuel stack, then the ventilation is set to the maximum rate of 3400 $m^3/h$. By this means, no significant damage has been caused to the installation.

## 2.5. Aerosol analysis

As in the previous experiments, the aerosol carried away with the combustion gases is sampled isokinetically in the exit duct with an array of 12 filters that are operated sequentially during and immediately after the course of the fire. The filters are routinely analysed for contaminant content by neutron activation of the europium in the low flux reactor of the German Centre for Cancer Research in Heidelberg (see (1) for more information).

Similarly, and as far as possible, the amount of contaminant remaining in the residue of the fire and on the test material plate (when this is non-combustible) is determined either directly or after wet decomposition as described in (1).

## 3. RESULTS AND DISCUSSION

### 3.1. Dry contamination

Tab.1 summarizes the data collected for an extensive series of experiments with the **"dry" contamination** process applied to the various glove box materials burned in or exposed to the flames of the standard PMMA fire. Various quantities of Ce-Eu-oxide powder, corresponding to the contamination levels 0.5 and 1.0 mg Ce /cm2, were spread only on the test plate (or sheet) and not on the PMMA.

For comparison purposes, it may be recalled that, as reported in (1), the mean values for contaminated PMMA were 1 to 2 % of original contaminant transported into the exit channel and 25 to 40 % left in the residue.

To the data of Tab.1 the following observations can be made :

- Significant particle transport from metallic surfaces shows the importance of turbulence as resuspension mechanism in large scale fires. On the other hand, it is evident that painting a surface does not affect the spreading of the contamination in the case of a fire. Erratic results for aluminium seem to be caused by early collapse of the metal plates and subsequent falling down of the contaminant powder in the burning PMMA.

- Among the plastic materials, the (relatively homogeneous) results for polycarbonate, polyethylene and PVC are in contrast to those for contaminated PMMA. The difference might be due to the different softening and burning characteristics of these materials. In the case of PMMA, the extensive formation, just below the burning surface, of bubbles filled with pyrolysis products and then migrating up the temperature gradient to the surface where they burst, was investigated in small-scale fire experiments (2), (3) and (4) and is regarded as a primary mechanism for particle ejection. No comparable mechanism could be observed in the case of polycarbonate and PVC which ignite poorly and char to a rigid surface crust. In these cases, only turbulence is likely to act as a resuspension mechanism.

- The analysis of the residue was considered too cumbersome in some cases, such as for polycarbonate which leaves a voluminous and hard residue, or for neoprene which burns quasi flashlike and entirely.

In conclusion, the data of Tab.1 show that, in general and with the important exception of the rubber materials used for gloves (neoprene and hypalon), the percentage of heavy metal transported into the ventilation outlet is not higher than with PMMA. Furthermore they show the superiority of polycarbonate (moreover much less combustible than PMMA) as construction material for glove boxes.

### 3.2 Wet contamination

Two series of experiments were carried out applying the "wet" contamination process (deposition and evaporation of solutions): first a series of 7 fires where the five PMMA plates of the standardized fuel assembly were contaminated, allowing a direct comparison with the results of the first report, then a series of fires involving the other contaminated materials according to the same procedure as above, i.e. using the PMMA fuel stack only as a fire source. The data from both series are collected in Tab. 2 and show that, in all cases, the percentage of heavy metal carried away into the ventilation outlet is significantly lower (by a factor between 5 and 10 for PMMA) than in the case of "dry" contamination.

This result suggests that the mechanisms determining the heavy metal resuspension are different in the two contamination processes. Not only are we dealing with different chemical compounds, but also the degree of attachment or even penetration of the particulates, on or into the substrate, seems to be much higher for the "wet" than for the "dry" contamination. In the latter case, the considerable turbulence accompanying the strong combustion, in the immediate vicinity of the fire and particularly in the strong updraught created especially in the chimney formed by the central holes in the stack of plates, likely acts as the main resuspension mechanism, which is also compatible with the observation of resuspension from completely inert surfaces such as stainless steel.

In the case of "wet" contamination, this turbulence mechanism might be much less effective in the resuspension of "captive" particulates.

## 4. MEASUREMENTS OF AEROSOL PARTICLE SIZE

A complete characterization of contaminated smoke from glove box fires also requires the measurement of the aerosol particle size distribution, since this determines to a great extent the atmospheric transport and inhalation characteristics of the aerosol. Two features make this measurement particularly difficult: in the first place the very low concentration of the heavy metal in the combustion gases with a maximum of about 30 $\mu g/m^3$ during the few minutes around the combustion peak (for a standard fire), secondly the relatively high concentration (up to 100 $mg/m^3$) of fluffy soot particles which rapidly tend to obstruct the sampling and back-up filters. Therefore the first measurements by means of usual small-volume impaction instruments (INSPEC or Andersen's cascade impactor) did not yield satisfactory results, except the evidence, confirmed by electron probe microanalysis (EPMA) of sampling filters, that the airborne Ce-Eu-oxide particles are not attached to the carbonaceous agglomerates in the smoke, but that they constitute a distinct aerosol population (1).

A new attempt was made with a high-volume Andersen's cascade impactor (mod. 234 SIERRA Instruments Inc.), directly connected to the ventilation exit channel and assuring isokinetic sampling by the type of the inlet nozzle. When operating at a nominal flow rate of 68 $m^3/h$, this apparatus fractionates suspended particulates into five aerodynamic size fractions with size cut-offs (50% collection) between 13.5 and 5.0 µm.

The previous observation, that the carbonaceous smoke particles are aerodynamically much smaller than the heavy metal carrying particles, was dramatically confirmed during these experiments. The large excess of carbonaceous particles, which were hardly deposited on the impaction stages, tended to clog the back-up filter, so that the sampling flow rate could not be maintained during the complete course of the fire. To overcome this difficulty, the sampling time was reduced to the interval of about 3 min. corresponding to the highest rate of heavy metal spreading as shown in the time sequence of a standard fire (see figure 2 of ref.1). Nevertheless the unavoidable drop of the flow rate from 68 to 50 $m^3/h$ seriously affects the accuracy. Another problem with this apparatus is the poor sensitivity of the measurement due to the relatively high europium background value (on the average 200 ng of Eu) of the collection substrate (a cellulose plate with a surface of 210 $cm^2$) for the impaction stages and of the back-up filter. The resulting detection

limit amounts to nearly 10 % of the average quantity of heavy metal normally re-suspended during the sampling time.

Taking into consideration the above remarks , only four experiments gave meaningful results and are reported in Tab. 3. They concern standard fires by which, for greater sensitivity, the PMMA fuel was contaminated with 150 mg of heavy metal per plate instead of the usual 75 mg. The contamination came from Ce-Eu-oxide powder in 3 cases and from Ce-Eu-nitrate solution in one case. In spite of the poor reproducibility, the following conclusions can be drawn from these results:

- A confirmation of previous observations: for both types of contamination sources, the particles carrying away the heavy metal are independent from and substantially bigger (aerodynamically) than the carbonaceous smoke particles which are nearly all collected on the back-up filter (cut-off size smaller than 5 µm).

- The heavy metal carrying particles originating from PMMA contaminated with powder are significantly bigger than those from PMMA contaminated with a dried solution.

## 5. CONCLUSIONS

The conclusions previously stated in the first step of this study can be completed as follows:

- In the event of a glove box fire, only a few percent of the radioactivity present as contamination inside the box remain airborne long enough, after dispersion, to leave the fire chamber by the ventilation outlet.

- The degree of radioactive air contamination, by resuspension of heavy metal during glove box fires, depends on the components that have burned or were exposed to the flames. The contamination dispersed is higher with polymethylmethacrylate PMMA, than with the other materials (e.g. polycarbonate) usually used for the construction and equipment of glove boxes, with the exception of rubber gloves.

- The activities dispersed from burning synthetic rubber gloves (both neoprene and hypalon) are somewhat higher than those from burning PMMA.

- Taking into account that PMMA is the major glove box construction material, the amount of contamination dispersed by a fire is lower (by about a factor 5) for fires involving "chemical" glove boxes, in which heavy metals have been handled only in aqueous solutions, than for fires involving glove boxes for fabrication or handling of nuclear fuels in form of powder or pellets.

- The particle sizes of heavy metal containing aerosols dispersed from burning contaminated PMMA depend of the source of the contamination. Contamination by aqueous solutions leads to smaller particles than contamination by powders.

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Tab. 1 Transport of heavy metal from fires involving plates of different materials contaminated with cerium-europium-oxide powder

| Type of contaminated material | | Percent of original cerium contaminant | | |
|---|---|---|---|---|
| | | Transported into ventilation exit channel | Left on the surface | Left in the residue |
| Stainless steel | (1) | 1.7 | 90 | * |
| Stainless steel | (1) | 0.2 | 86 | 0.3 |
| Stainless steel | (1) | 0.6 | 60 | 2.9 |
| Stainless steel | (1) | 0.5 | 58 | 0.5 |
| Painted stainless steel | (1) | 0.3 | 78 | 0.3 |
| Painted stainless steel | (1) | 2.0 | 62 | 0.4 |
| Aluminium | (1) | 2.8 | 14 | 8.9 |
| Painted aluminium | (1) | 2.1 | * | 20 |
| Painted aluminium | (1) | 2.3 | * | 29 |
| Polycarbonate (1.5 kg) | (1) | 0.5 | - | * |
| Polycarbonate (0.9 kg) | (1) | 0.4 | - | 63 |
| Polycarbonate (0.9 kg) | (1) | 1.4 | - | 46 |
| Polycarbonate (0.9 kg) | (2) | 0.2 | - | * |
| Polycarbonate (0.9 kg) | (2) | <DL** | | * |
| Polyethylene (1 kg) | (1) | 1.0 | - | 23 |
| Polyethylene (1 kg) | (1) | 1.3 | - | 42 |
| Neoprene (87 g) | (1) | 5.9 | - | 13 |
| Neoprene (32 g) | (1) | 2.3 | - | 19 |
| Neoprene (40 g) | (2) | 2.0 | - | * |
| Neoprene (35 g) | (2) | 3.4 | - | * |
| Hypalon (35 g) | (2) | 2.5 | - | 3.4 |
| Plywood | (2) | 0.8 | | 1.6 |
| Hard PVC (0.9 kg) | (2) | 0.4 | | 3 |
| Soft PVC (0.3 kg) | (2) | 0.3 | | 33 |
| In cardboard container: | | | | |
| Kleenex (0.3 kg) | | 0.7 | - | 57 |
| Kleenex (0.3 kg) | | 2.2 | - | 34 |

Cerium contamination level (1) 0.5 mg $cm^{-2}$ (2) 1.0 mg $cm^{-2}$
For Kleenex, total contamination 500 mg Cerium
(*) not measured
(**) the detection limit amounts to 0.1 %

Tab. 2 Transport of heavy metal from fires involving plates of different materials contaminated by evaporation of a cerium-europium-nitrate solution

| Type of contaminated material | | Percent of original cerium contaminant transported into ventilation exit channel |
|---|---|---|
| PMMA (Five Plates) | (1) | < DL* |
| " " | (1) | 0.5 |
| " " | (2) | 0.3 |
| " " | (2) | 0.25 |
| " " | (2) | 0.5 |
| " " | (2) | 0.7 |
| " " | (2) | < DL |
| Polycarbonate | (4) | < DL |
| " | (4) | < DL |
| Neoprene | (3) | 0.3 |
| Hard PVC | (3) | 0.4 |
| Wood | (3) | 1.1 |
| Kleenex (in cardboard container) | | < DL |
| Stainless steel | (3) | < DL |

Cerium contamination level
(1) 0.1 mg cm$^{-2}$
(2) 0.2 mg cm$^{-2}$
(3) 1.0 mg cm$^{-2}$
(4) 2.0 mg cm$^{-2}$

(*) the detection limit amounts to 0.1 %

Tab. 3 Particle size analysis of heavy metal particles spread from burning contaminated PMMA

| Experiment Number<br>cut-off size Dp 50 (µm) | Cumulative mass percent of crium in particles smaller than cut-off size | | | |
|---|---|---|---|---|
| | Contamination from Ce-Eu-oxide powder | | | Contamination from Ce-Eu-nitrate solution |
| | 1 | 2 | 3 | 4 |
| 13.5 | 73 | 60 | 59 | 84 |
| 8.0 | 44 | 37 | 30 | 76 |
| 6.1 | 35 | 21 | 17 | 68 |
| 5.0 | 32 | 13 | 9 | 61 |

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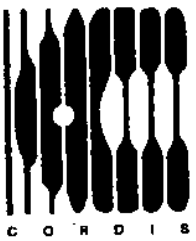


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The present Part II completes the study with comparative fire experiments involving contaminated samples of various glove box materials burning in or exposed to the flames of the standardized 0.6 MW fire source previously developed. Beyond spreading of the Ce-Eu oxide powder as mentioned above, the other important surface contamination process is used, i.e. deposition and subsequent drying of droplets from acid cerium-europium solutions.

It is shown that, among the tested materials, and with the exception of synthetic glove rubber, burning PMMA spreads the most radioactive contamination. On the other hand, this potential risk is much lower for fires involving materials contaminated from solution deposition than from powder or pellets.

Attempts to measure the airborne contaminant particle sizes did not yield conclusive results. They suggest, however, that contamination from solutions leads to smaller heavy metal containing aerosol particles than contamination from powders.

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